

RELIABLE CHEMICAL DETERMINATION OF OXYGEN-CONTAINING  
FUNCTIONALITIES IN COAL AND COAL PRODUCTS.  
CARBOXYLIC ACID AND PHENOLIC HYDROXYL FUNCTIONALITIES

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## INTRODUCTION

Coal contains various chemical functionalities. Particularly, the oxygen-containing functionalities are considered to play an important role to control its physical and chemical properties. Recent development of sophisticated instrumentation such as FT-ir,  $^{13}\text{C}$ -CP-MAS-NMR, XPS, etc., for the direct non-destructive characterization of a solid coal has made it possible to provide quite reliable information about such hetero-atom-functionalities as sulfur-(1), nitrogen-(2) and oxygen-containing functionalities. However there still seems to be a problem concerning the selectivity between delicate functionalities, i.e., a carboxylic, phenolic and alcoholic hydroxyl functionalities.

About 40 years ago, Blom et al.(3) developed chemical determination methods for various oxygen-containing functionalities in coal and coal products, which have often been used in the literature with some minor modifications. In the course of our studies concerning the solvent swelling of coal, we have learned that this classical method may involve serious experimental errors based on the accessibility, particularly the determination of the carboxylic acid functionality in coals, which used to be carried out in an aqueous solution by using calcium acetate. In general, the coal does not swell very much in a water, furthermore the coals exhibit significant steric requirements for the penetrant molecules(4), and its extent of swelling widely varied depending upon the coal rank(5). Usually, a higher rank coal like a bituminous coal exhibits serious penetration restriction. Thus, if one wants to use a chemical reaction on coals, in order to obtain reasonable accessibility of chemical reagent to the functionality in solid coals it is critical to pay maximum attention to the arrangement of the reaction conditions, i.e., reagents and solvents.

Based on our experimental results of coal swelling, we have developed a quite reliable chemical determination method for carboxylic acid and phenolic hydroxyl functionalities in coal and coal products. The principle of this method is described as follows: Chemical reactions using various borohydrides were adopted for the determination of these functionalities as shown below, which have very different reactivities and give us a stoichiometric amount of hydrogen gas for each functionality in a pyridine solvent. Thus, we can discriminate each functionalities based upon the difference of their reactivities to the borohydrides:



(R = Aryl, Alkyl, -CO-, H, etc.; M = Li, Na, K, n-Bu<sub>4</sub>N etc.)

## EXPERIMENTAL

The chemical reagents were commercial products (Aldrich's gold label grade) which were used without further purifications. Pyridine was dried over calcium hydride and distilled before use. Coals from the Ames Coal Library were ground, seized, dried at 110°C under vacuum overnight, and stored under a dry nitrogen atmosphere. The pyridine extractions of coals were carried out by using excess amount of pyridine under an ultrasonic irradiation. In order to remove trace amounts of pyridine in the pyridine-extract it was washed by THF/H<sub>2</sub>O(30vol%) solution saturated by CO<sub>2</sub>, then dried at 110°C overnight, and stored under a dry nitrogen atmosphere.

Volumetric measurements of hydrogen gas evolved through the reactions were carried out by using a gas-buret under hydrogen atmosphere at 25°C. A typical procedure was as follows: Pyridine-extract(0.1g) was thoroughly ground by using an agate mortar in a dry-box, and placed into a 30ml reaction vessel. Dry pyridine(5ml) was added and the mixture stirred for 30-60 minutes prior to start the reaction with excess amount of pyridine/tetra-n-butylammonium borohydride solution. The volume of hydrogen gas generated from the reaction mixture was measured by a gas-buret.

## RESULTS AND DISCUSSION

### 1. Reactivities of various borohydrides toward hydroxyl functionalities

In order to evaluate the chemical reactivity of borohydrides, 1-naphthol was chosen as a standard model compound of a phenolic hydroxyl functionality. In Figure 1, the effects of the counter cations of borohydrides are demonstrated. This Figure shows the rate of completion of the reaction vs. reaction time in minute, which were calculated from the volume of the hydrogen gas evolved. Very interestingly, a lithium borohydride reacted very rapidly(completed within 5 minutes under these reaction conditions), compared to the others which were finally complete only after a prolonged reaction time. Among the experimental data shown in this Figure, it is also quite interesting to note that tetra-n-butylammonium borohydride reacted with 1-naphthol slowly and stoichiometrically, since the affinity of these types of tetra-alkyl ammonium compounds for the macromolecular network structure of coals had been well-known to be quite high, i.e., Liotta Methylation(6). There will be a good chance to distinguish kinetically between a phenolic hydroxyl functionality and more stronger hydroxyl functionalities like a carboxylic acid in a solid coal.

## 2. Reactions of lithium borohydride with various hydroxyl model compounds

The reactivities of various hydroxyl functionalities toward lithium borohydride were examined by using model compounds, such as a water, benzyl alcohol, 1-naphthol, catechol and benzoic acid. Figure 2 summarizes the results.

Very interestingly, the reactions with carboxylic acid (benzoic acid) and phenolic compounds (1-naphthol and catechol) proceeded significantly faster than those of others (benzyl alcohol and water), which means that the amount of hydrogen gas evolution within 60 minutes under this reaction condition represents the amount of both carboxylic acid and phenolic hydroxyl functionalities.

## 3. Reactions of tetra-n-butylammonium borohydride with various hydroxyl model compounds

Figure 3 shows the results obtained from the experiments to examine the reactivities of various model compounds toward tetra-n-butylammonium borohydride.

Compared to the previous experiments with lithium borohydride, the reaction rate of benzoic acid was significant. Most of the hydrogen gas evolution at the initial stage of the reaction is considered to come from the reaction with a carboxylic acid functionality. Even if it was a mixture of those, we can obtain reasonable analytical values of the acid functionality by a treatment of an extrapolation of the curve in the Figure.

## 4. Quantitative determination of carboxylic acid and phenolic hydroxyl functionalities in the mixture of various hydroxyl model compounds

Coal is believed to contain various hydroxyl functionalities, such as a water, alcoholic, phenolic and carboxylic hydroxyl functionalities. Based on the results described above, we have tried to evaluate the proposed method, "Metal hydride method" using a mixture of the model compound which was prepared with an equivalent amount of the functionalities. Figure 4 exhibits the hydrogen gas evolution from reaction mixtures for both the case of the lithium salt and tetra-n-butyl ammonium salts. The data shown in this Figure seem to be consistent. The equilibrium value of the reaction (hydrogen gas evolution) with lithium salt must represent the sum of carboxylic acid and phenolic hydroxyl functionalities, meanwhile in the case of tetra-n-butylammonium salt the extrapolated value must be the amount of carboxylic acid functionality. Obviously, the data shown in this Figure seems to be consistent.

## 5. Quantitative determination of carboxylic acid and phenolic hydroxyl functionalities in the pyridine-extract of coal

In order to minimize the complications of the accessibility of the borohydride molecule to the active sites buried into the macromolecular network structure of coal and inorganic components in coal, we have started the quantitative determination of these functionalities by using pyridine-extract which gives us a homogenous reaction system. In Figure 5, a typical measurement is demonstrated, in which Illinois No.6 coal was used. Although the rate of the hydrogen evolution seems to be slow compared to those of the model compounds, the pattern was quite similar. The calculated values of the contents of carboxylic acid and phenolic hydroxyl functionalities from the Figure 5 were 0.82 mmol/g and 2.03 mmol/g which corresponded to 8 units/660-carbon atom and 24 units/660-carbon atom. Although we have no reason to believe that the content of these functionalities in the pyridine-extract is exactly same as the raw coal, it is quite interesting that the content of phenolic hydroxyl functionality was almost equal to the number (25 units/660-carbon atom) of phenolic hydroxyl functionality described in the Shinn Model (7) of Illinois No.6 coal. But there was 8 fold differences in the carboxylic acid functionality (1 unit/ 660 carbon atom in Shinn Model vs. 8 units/660 carbon atom by present work).

Table 1 summarizes the analytical data obtained by this new method for the pyridine-extracts of different rank of coals. The coal-rank dependency of each functionalities appearing in this Table seem to be unusual, based on our previous understanding. The carboxylic acid functionality (which had been believed to be so reactive that it would not survive metamorphism and be detectable in higher ranks of coal) seems to exist significantly in a wide range of coals. On the other hand, the phenolic hydroxyl functionality in coal is reasonably stable over the coal-rank range used in this study. The contradictions on these data revealed here are thought to prove very serious and important problems in reviewing our understanding of the physical and chemical properties of coals.

The accumulation of the experimental data concerning the content of these functionalities in the raw coals is now underway in our laboratory. We are now developing the method for the determination of an alcoholic hydroxyl functionality in coal.

## CONCLUSION

Based on the experimental results of solvent swelling of coal, a reliable chemical determination method both carboxylic acid and phenolic hydroxyl functionalities has been developed by using the reactions of borohydride salts in pyridine solvent. Advantages of this method are considered to be (a) better accessibility of chemical reagent into the macromolecular network of coal (in pyridine solvent), (b) quantitative and direct (one-step) reaction, and (c) accuracy and easiness (volumetric determination of hydrogen gas).

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Table 1. Contents of carboxylic acid and phenolic hydroxyl functionalities in pyridine-extract of coals

Coal	Carbon content(% dmmf)		Content of functionality(mmol/g)	
	Raw coal	Pyridine-extract	-COOH	Ar-OH
Hanna No.80	73.1	77.4	0.96	2.04
Adaville No.11	76.6	76.0	1.02	2.08
Illinois No.6	80.6	79.7	0.82	2.03
West Kentucky No.9	82.5	79.9	0.65	1.45
Pittsburgh No.8	85.1	77.8	0.52	1.58

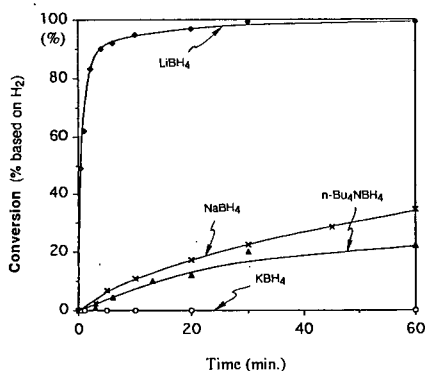


Figure 1. Reactions of 1-naphthol with various borohydrides

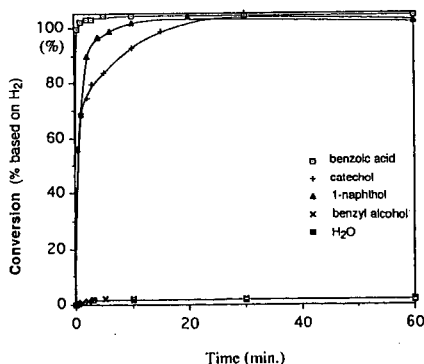


Figure 2. Reactions of  $\text{LiBH}_4$  with various model compounds

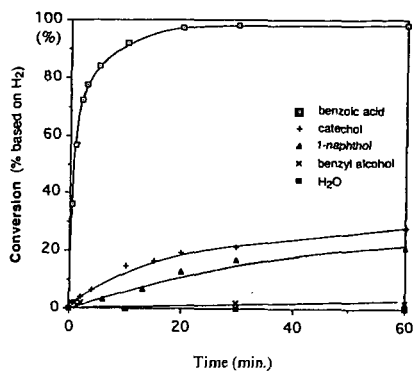


Figure 3. Reactions of  $n\text{-Bu}_4\text{NBH}_4$  with various model compounds

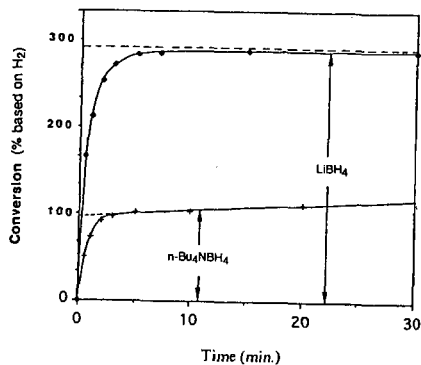


Figure 4. Reactions of  $\text{LiBH}_4$  and  $n\text{-Bu}_4\text{NBH}_4$  with model compounds mixture (benzoic acid / catechol / 1-naphthol / benzyl alcohol /  $\text{H}_2\text{O} = 1/0.5/1/1/1$  mol.)

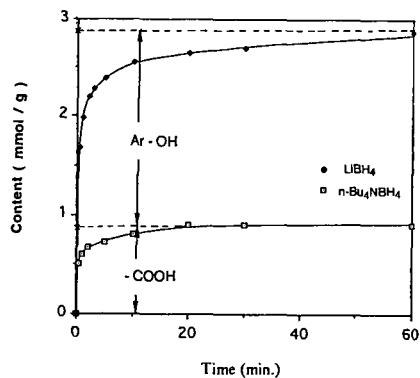


Figure 5. Determination of carboxylic acid and phenolic hydroxy functionalities in pyridine-extract of lillinsol No. 6 coal